Investigation of the Change in Hydrophobicity of Polycarbonate in Atmospheric Pressure Dielectric Barrier Discharge (APBDB) Generated with a 50 Hz Power Supply

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Abstract
Dielectric Barrier Discharge (DBD) of disc electrodes with diameter 5 cm and thickness 1 cm of each has been used for treatment of the samples. The discharge was produced at fixed inter-electrode gap of 4.5 cm for the study of effectiveness of treatment on the surface of the Polycarbonates (PCs). After the treatment in varying time periods the hydrophobic properties of sample changed to the hydrophilic. To investigate the effect of plasma treatment, contact angle was measured by using goniometer with water as a testing liquid. Effect on the sample due to treatment time, applied voltage and working gas were studied. Treatment carried out in Argon environment produced better wettability compared to atmospheric air. Aging effect was also studied to see the evolution of the wettability after time elapsed by measuring the contact angle up to one month after the treatment. Contact angle was increased from 39.35^o C to 56.4^o C, which was still very lower than the contact angle 81.2^o of untreated sample.

Key words: *Atmospheric Pressure Dielectric Barrier Discharge (APDBD), Polycarbonates, Ageing, Functional groups, Non- equilibrium Plasma, Reactive species, Surface energy, sessile drop technique.*

Introduction

Plasma is considered as the fourth state of matter next to solid, liquid, and gas. The term plasma was introduced by Langmuire in 1928 to describe the state of matter in the positive column of glow discharge tube. But the existence of plasma as the fourth sate of matter was first identified by Sir William Crookes in 1879. Though it is common to stars and sun as 99% of our universe contains plasma, it is rarely found on the earth's surface [0]. The reactive species on the plasma are ions, electrons, neutral particles and UVs which plays very important role for the surface treatment of the materials. In technical applications, plasma have been created for a long time – for instance in the manufacture of fluorescent lamp, television screen, etc. Nowadays plasma technology is used in various fields such as plasma medicines, surface modification of materials, water treatment, thin film deposition *etc*.

In this study, PC samples were treated in Atmospheric Pressure Dielectric Barrier Discharge (APDBD) using low (50 Hz) frequency in atmospheric air and air argon mixture. Surface characterizations were performed using contact angle measurements, surface free energy measurements and ageing effect.

DBD (Dielectric Barrier Discharge)

Dielectric Barrier Discharge (DBD) is one of the methods of producing the non-equilibrium plasma at atmospheric pressure. It is also referred to as barrier discharge or silent discharge. DBD is the system in which discharge takes place between the metallic electrodes which have been separated in the order of mm and with alternative driving voltage typically 10 kV or more, and at least one of the electrodes is covered with a dielectric material like ceramics, glass, quartz plate, poly carbonates as shown in Fig.1**.** For this purpose metallic electrode with dielectric coating i.e. enamel layer can be used. Typically very high voltage of 33 kV/cm is required to ionize the gas particles between the electrodes [0]. It is widely used non-equilibrium plasma source usually in ozone generation, plasma medicine and surface modification. The generation of powerful coherent infrared radiation in CO_2 lasers and of incoherent VUV or UV excimer radiation in excimer lamps is two examples that became commercially available within a few years. Biologically, it is also used in bacterial inactivation and medicine.

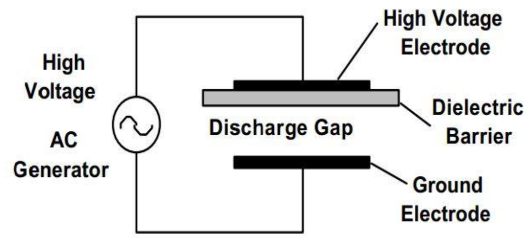


Figure 1: Schematic diagram of Dielectric Barrier Discharge with single electrode

EXPERIMENTAL SET-UP

A DBD system with disc electrodes made from brass, having same thickness and radius were used for the generation of plasma in the study. Upper electrode was movable and lower one was fixed. The discharge was produced between the electrodes. The samples were treated in the discharge which was produced between the upper electrode and barrier. Plasma was produced at atmospheric pressure in air and air-argon mixture. The gap between the electrodes was maintained fixed. Polycarbonate sample was treated on different time and voltage to observe the effectiveness of the plasma treatment. Effectiveness of the treatment in all samples was investigated measuring contact angle with a goniometer.

Discharge was generated in a parallel plate disc electrode system powered by high tension AC source. Two metallic electrodes with diameter 5 cm and thickness 1 cm were used for the fabrication of the DBD system. A glass plate having thickness 2mm was used as a barrier between the electrodes. The DBD characteristics can mainly be controlled by the AC input voltage, input frequency, inter-electrode gap, nature of dielectric material, temperature, moisture, working gas pressure and gas flow rate. The schematic diagram for the DBD is shown in Figure 1, which consists of two disc electrodes, made from brass, held horizontally parallel. Glass was used as a barrier between the electrodes to avoid the formation of arc in the discharge. The inter-electrode gap was maintained at 4.5 mm which includes thickness of the dielectric barrier. The electrode system was fixed inside the cylindrical glass tube as shown in Figure.

In order to study the effect of the plasma treatment, we measured the contact angle as a surface characterization . To prevent the treated sample from contamination from ambient, it was placed inside the closed glass box and contact angle was measured immediately. Wetting was characterized by the contact angle measurement of sessile drop (4 ml, testing liquid as water). The surface energy of the sample was calculated by using Owen's and Wendt model [0]. For the measurement of the contact angle, rame-hart goniometer, model: 200, was used.

Samples were kept on the dielectric barrier and treated for different times; 20 s, 40 s, 1 min, 2 mins, 5 mins, 8 mins and 10 mins. The discharges were produced under the variable voltages of 11.7 kV, 15.5 kV and 19.5 kV. Transformer with voltage controller was used to control the applied voltage to the reactor. The mixture of air-argon gas was also used to study the effect of the gas on plasma treatment of polycarbonate at 11.7 kV.

RESULT AND DISCUSSION

Effect of treatment

The sample PC was hydrophobic before treatment and changed to hydrophilic after treatment as shown in figure 2. Treatment time was varied from 0-10 mins and the respective contact angles were measured.

Figure 2: Water drop on the a) untreated sample surface and b) plasma treated sample surface

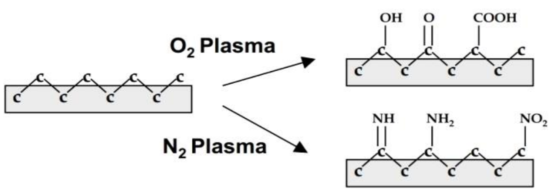
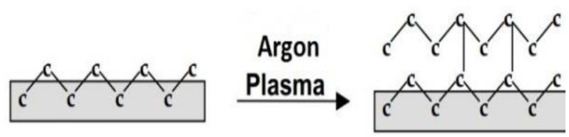


Figure3: Schematic diagram showing the functional group after atmospheric plasma treatment



igure 4: Schematic diagram showing new chain of arbon after argon plasma treatment

The contact angle of untreated surface was 81.4^0 and its value decreased after the plasma treatment. The value of contact angle decreases remarkably and remains almost constant thereafter. It indicates that a level of saturation is achieved after 20 s. This saturation could be attributed to the saturated bond between the carbons of polycarbonate.

Similarly, the increase in surface energy was also significant in the first 20 s but afterwards it increased slightly, and achieved saturation thereafter. Similar types of results have been reported in [4, 5, 0]. It has been reported that plasma treatment leads to an increase in adhesive strength of the sample. The increase was attributed primarily to the bonding of Oxygen atoms to the polymer surface as in figure 3.

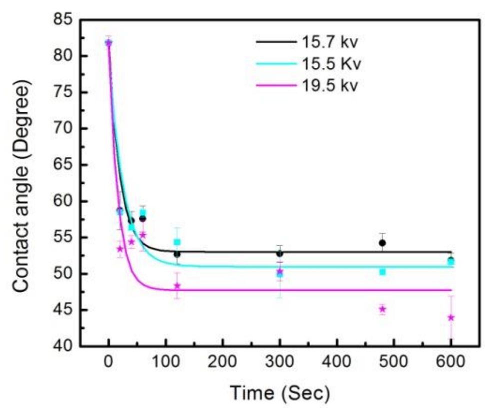


Figure 5: Variation of contact angle with treatment time at different potentials

Exposing polymer on the plasma produces two simultaneous effects: first, etching due to the reaction of atomic oxygen with carbon of surface giving volatile product and second, and formation of functional groups on the polymer surface due to the interaction of active species in the plasma and polymer surface. The surface energy of the sample increases due to the change in functional group of the carbon chain in the polymer [0].

Atmospheric air plasma produces a variety of hydrophilic functional groups including C-O-C (ether), C=O (Carbonyl), C-O-O (Peroxide), NH (Amine), NH_2 (Amino), COOH (Carboxyl), N=C=O (isocyanate) as in Fig. that increases the wettability of poly-carbonate [0] since atmospheric air mostly contains nitrogen and oxygen gases. Hence, oxygen and nitrogen play the important role on the surface modification [0]. On the other hand, argon plasma treatment produces purely physical surface modification without added functional group on the surface as in figure 4. The direct and relative energy transfer causes the surface modification of the PC. Another factor for the surface modification is UV radiation emitted by plasma. On exposing Polycarbonate to the argon plasma, it breaks the C-C or C-H bonds and produces the free radical near the surface, and eventually plasma removes the low molecular weight species and converts it to the high molecular weight species. Argon plasma treatment modifies the surface because of the cross linking of the PC and sputtering of the material [0].

Surface characterization of the samples

PC samples treated in the discharge were subjected to surface analysis by measuring contact angles. Significant changes in contact angle and surface energy were observed. We maintained the fixed inter-electrode distance in all our experiment as per our objective.

Increase in the wettability suggests the increase in the surface free energy of the PC. In our experiment, we measured the contact angle to calculate the surface free energy of the plasma treated and untreated samples. The surface energy of virgin sample was 35 mJ/m^2 but after the first 20 s of exposure time it climbed to 50

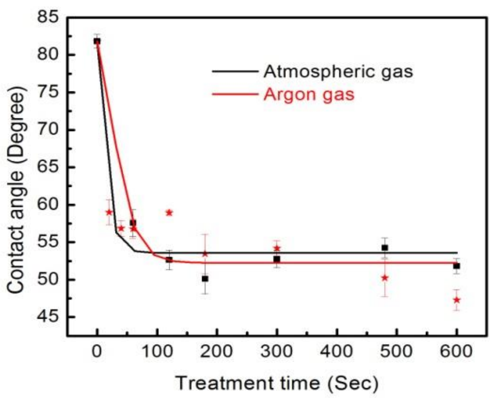


Figure 6: Variation of contact angle with treatment time at different gas mixture

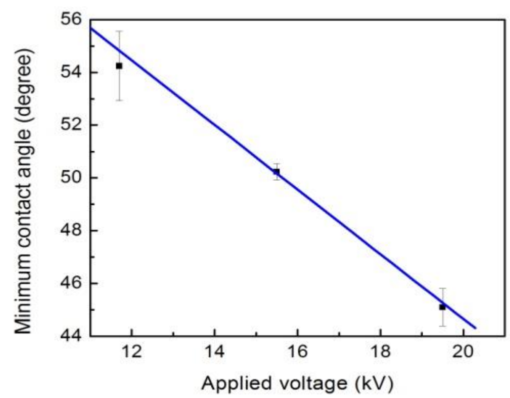


Figure 7: Variation of maximum Contact angle with applied voltages

mJ/m^2 and remains almost constant even after the 10 minutes of further treatment on atmospheric air. But it is interesting to note that saturation point in air-argon plasma is significantly more than in atmospheric air plasma which is shown in Figure 6.

The surface free energy enhances due to the introduction of the polar functional groups on the surface of the PC by the plasma treatment. Contact angle of water drop on polycarbonate sample reduced more in air-Argon plasma than in air plasma because of the cross-linking via activated species of inert gases (He or Ar). Inert gas plasma or noble gas plasma creates the effective free radicals but does not add new chemical functional groups as in the case of oxygen or nitrogen plasma [0] Different factors such as power, inter electrode distance, working gas, applied voltage, frequency, treatment time, etc. also affect the surface treatment. Here, we were only concerned with the working gas, treatment time and applied voltage. From our observation, there was measurable change in the surface energy on varying the applied voltage and working gas.

Effect of applied voltage in wettability

For the production of plasma at atmospheric pressure, high potential of the order of kilovolt was required. Step-up transformer was used to increase the voltage. Significant change was observed in the hydrophilicity of the samples treated in the discharge with the applied voltages; 11.7kV, 15.5 kV and 19.5 kV. Figure10 gives the comparative study of the effect of the applied voltages on the hydrophilicity of Polycarbonate.

It is seen that in first 60 s, contact angle decreased from 81.4^o to 57.57^o on 11.7 kV of applied voltage. More significant effect was observed in higher potential; more noticeable results were observed in 19.5 kV than in 15.5 kV. After the further treatment up to 10 min, contact angle decreased to 43.95^o at 19.5 kV, which is approximately 8^o less than the sample treated in 11.7 kV. Therefore, we observed the linear relation between the applied voltage and minimum contact angle attained which is shown in Figure 10. However, very high potential was difficult to handle because of the arc produced between the electrodes.

Stability of modified surface (Ageing)

The process of evolution of original characteristics with the time elapsed after plasma treatment is called aging. In the present work, aging is studied in the duration of one month by measuring contact angle at different aging time: instantly, 30 mins, 1 hr, 3 hrs, 1 day, 3 days, 12 days and 29 days after plasma treatment. The contact angle of the sample after treatment was 39.35^o and scaled up to 45^o after 30 minutes of the storage time. The effect of aging on contact angle is shown in the Fig. The value of the contact angle started to restore gradually, reaching 56.4^o after 29 days, but was still much lower than the original value even one month after the treatment.

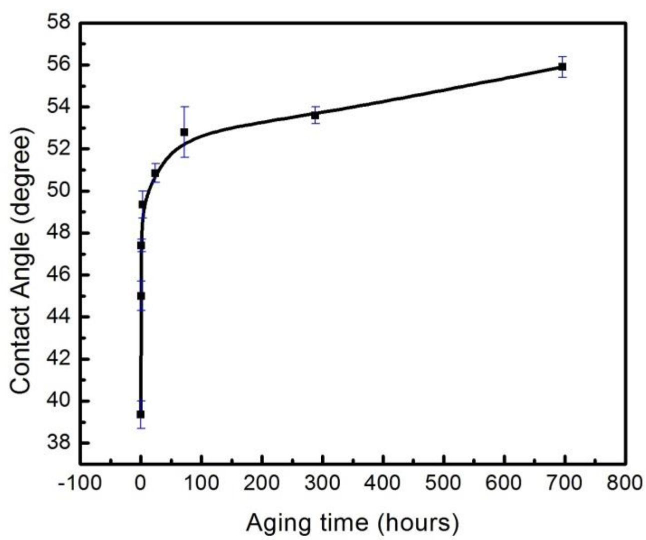


Figure 8: Contact angle as a function of aging

As we treat the sample by plasma, treatment not only modifies the surface but also leaves active radicals at the surface which causes the subsequent reaction to the surroundings causing the gradual recovery of the original hydrophobicity. Often the hydrophilicity obtained is lost with time elapsed, depending on the temperature and other environmental (storage) conditions [0].

Conclusion

Sample surface became hydrophilic after the treatment on atmospheric pressure DBD. Contact angle rapidly decreased from 81.4^o to 58.54^o within 20 seconds of treatment and almost constant on further treatment. Prominent effect was seen on using air-argon mixture, and applied voltage. Aging effect study has also showed the significant change in surface properties on the increment of aging time.

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